Indian J. Phys. **77A (6)**, 553-559 (2003)

AN INTERNATIONAL JOURNAL
IJPA

Magnetic relaxation in nano-particles : a Mössbauer study

K K P Srivastava
Department of Physics, T M Bhagalpur University, Bhagalpur-812 007, Bihar, India
E-mail : kkp44@yahoo.com

Abstract : Ultra-fine superparamagnetic particles of iron compounds with size 50 to 125 Å probed through Mössbauer spectroscopy usually show magnetic relaxation effects at low temperatures. A magnetic sextet is observed for long relaxation times compared to nuclear lifetime whereas the magnetic interaction disappears for short relaxation times and this change usually occurs between 25 to 100 K. A theoretical model has been developed for the magnetic relaxation process considering that on microscopic level it involves an exchange of energy between magnon and phonon sub-systems *via* magnon-phonon scattering induced by dynamic exchange. It is seen that the relaxation rate increases with temperature in a complicated manner besides its dependence on the number of magnetic ions or particle-size. The calculated rates appear consistent with the observed Mössbauer results at low temperatures for some of the iron oxides

Keywords : Nano-particles, superparamagnetic relaxation, magnon-phonon interaction, Mössbauer study

PACS Nos. : 76.30.Fe, 76.80.+y

1. Introduction

The Mössbauer spectra of nano-size particles of α-Fe_2O_3, Fe_3O_4, ferrihydrite, ferritins *etc* [1–3] often show temperature dependent magnetic relaxation. Such particles are known as superparamagnets and thermal fluctuation of their magnetization is called superparamagnetic relaxation. The shape of the magnetic hyperfine spectra depends upon the rate of fluctuation (relaxation rate) of the magnetization vector along possible directions, and its effect can be observed only when the relaxation time (*i.e.* inverse of relaxation rate) is comparable to the life time of the nuclear decay. For ^{57}Fe nucleus this window of observation lies between 10^7 to 10^9 sec^{-1}. At relaxation rates below the lower limit one observes a magnetic sextet and for rates above the upper limit the magnetic interaction is washed out.

In the standard theory for particles with uniaxial symmetry the magnetization vector randomly jumps between two directions ($\theta = 0, \pi$) corresponding to the energy minima of the system given by [4] :

$$E = -KV \cos^2\theta - HM_S \cos\theta, \quad (1)$$

where K = anisotropy energy per unit volume, V = volume of the particle, M_S = net magnetization of the particle, θ = angle between the magnetization vector and the anisotropy axis and H = applied field along anisotropy axis. The theories given by Brown [4] and Aharoni [5] treat the problem basically as flip-flops between two directions ($\theta = 0, \pi$) separated by the anisotropy potential barrier (KV) and the relaxation rate is given as :

$$r = r_0 \exp(-KV/k_BT) \quad (2)$$

where the pre-exponential factor r_0 is taken to be of the order of 10^{10} to 10^{11} sec^{-1}. Quite often the same is also written in terms of relaxation time (τ) as :

$$\tau_0 \exp(KV/k_BT) \quad (3)$$

where the pre-exponential factor τ_0 may be of the order of 10^{-10} to 10^{-11} sec. It is relevant to mention that for small magnetic particles or micromagnets the anisotropy energy basically arises from 'exchange anisotropy' and 'shape anisotropy'. The exchange anisotropy is an interfacial effect between two magnetic subsystems specially where the interaction is between an antiferromagnetic and a ferromagnetic material, whereas the shape anisotropy is related to surface effects [6].

In an earlier paper, Jones and Srivastava [7] had considered the many-state relaxation model by including all possible orientations of M_S and obtained the expression for Mössbauer line shape function using the stochastic theory of Blume and Jones [8]. In a special case the many-state relaxation model reduces to Brown's two level picture [4]. However, the basic limitations of the existing theories is the absence of any description of the microscopic process which is responsible for causing superparamagnetic relaxation and this point was also emphasized earlier [9,10]. Until now the interaction between the particle and its environment has been expressed in terms of a rapidly fluctuating random magnetic field which is inadequate from a microscopic point of view. Even classically it is difficult to quantify such random magnetic fields and their temperature profile.

It is therefore desirable to develop an interaction Hamiltonian (or perturbation potential) which produces superparamagnetic relaxation and naturally such an interaction should take into account the dynamics of spin fluctuations and lattice vibrations. This leads to a coupling between spin waves and lattice waves (or magnon-phonon coupling) and Akhiezer [11] has discussed its importance for magnetic crystals at low temperatures. It represents the thermal modulation of the Heisenberg exchange due to lattice vibrations, which produces an exchange of energy between magnon and phonon sub-systems and magnetic relaxation. The method developed by Akhiezer [11] and used by Sinha and Upadhyaya [12] for iron compounds will be followed with necessary approximations relevant to the system.

2. Dynamic exchange interaction

The five $3d$-orbital functions of an Fe atom under octahedral or cubic crystal field are well known. In Fe(3+) each orbital is occupied by one electron that gives ^6S ionic state. The exchange integral between two electrons of the neighboring ions is given by :

$$J_0(R_{mn}^0) = \langle \Phi_{\alpha,m}(r_1)\, \Phi_{\alpha,n}(r_2) \mid (e^2/r_{12}) \mid \Phi_{\alpha,n}(r_1)\, \Phi_{\alpha,m}(r_2) \rangle \quad (4)$$

where Φ_α is a crystal field orbital, r_1 and r_2 are the spatial positions of the two electrons, $r_{12} = r_1 - r_2$, R_n^0 and R_m^0 are the positions of n-th and m-th ions, and $R_{mn}^0 = R_n^0 - R_m^0$. The exchange interaction, which gives rise to magnetic ordering, is given by :

$$H_e = -2\sum J_0(R_{mn}^0) S_m . S_n , \quad (5)$$

where S_m and S_n are the spins of m-th and n-th ions, and the summation extends over nearest neighbors.

The lattice vibrations produce an oscillating crystal field potential V' given by :

$$V' = \sum (\partial V/\partial R_{mn})_0\, dR_{mn} \quad (6)$$

where $R_{mn} = R_{mn}^0 + dR_{mn}$. It can mix an excited orbital state into the ground $3d$-orbital state that modulates the exchange interaction. The modified orbital wave function can be given by [12] :

$$\Psi_\alpha = \phi_\alpha + \sum (\langle \phi_\alpha \mid V' \mid \phi_\beta \rangle)/(E_\alpha - E_\beta), \quad (7)$$

where E_α and E_β are the energies of the states ϕ_α and ϕ_β, and the summation extend over β. In the present case ϕ_α is a $3d$-orbital and ϕ_β will be an empty $4p$-orbital of Fe(3+). For the modified wave function the exchange integral takes the form :

$$J(R_{mn}) = J_0(R_{mn}^0) + J'(R_{mn})\, dR_{mn},$$

where

$$J'(R_{mn}) = 4 \sum \langle \Phi_{\alpha,m}(r_1)\, \Phi_{\alpha,n}(r_2) \mid (e^2/r_{12}) \mid \Phi_{\alpha,n}(r_1)\, \Phi_{\beta,m}(r_2) \rangle \times \langle \Phi_{\beta,m}(r_2) \mid (\partial V/\partial R_{mn}) \mid \Phi_{\alpha,m}(r_2) \rangle / (E_\alpha - E_\beta). \quad (8)$$

Hence the dynamic exchange is expressed as :

$$H'_e = -2\sum [J'(R_{mn}) dR_{mn}] S_m . S_n , \quad (9)$$

This interaction is responsible for the coupling between electronic spins and lattice vibrations in a magnetically ordered crystal.

3. Magnon phonon interaction

The magnon-phonon interaction Hamiltonian is obtained by expressing the ionic displacements in terms of phonon operators and the spin operators in terms of magnon operators. Using Holstein-Primakoff formalism [13,14] one may write as :

$$S_+^m = (2S/N)^{1/2} \sum \exp(-iq.R_m^0) b_q ,$$

$$S_-^m = (2S/N)^{1/2} \sum_{q'} \exp(iq'.R_m^0) b_{q'}^*,$$

$$S_z^m = S - (1/N) \sum_{q,q'} \exp[i(q'-q).R_m^0] b_{q'}^* b_q ,$$

where b_q and $b_{q'}$ are magnon annihilation and creation operators, q and q' are magnon wave vectors, S is spin of each ion and N is the number of magnetic ions under magnon excitation. Similar transformations can be written for the n-th ion at R_n^0. Using these relations one obtains that :

$$S_m.S_n = (1/2)\ (\ S_+^m.S_-^n + S_-^m.S_+^n) + S_z^m.S_z^n$$

$$= S^2 - (S/N) \sum_{q,q'} [\exp(-iqa) - 1][\exp(iq'a) - 1] b_{q'}^* b_q \quad (10)$$

where $R_n^0 - R_m^0 = a$ is the separation between nearest neighbors (or lattice constant) and the m-th ion is supposed to be at the origin. After summation the terms in (9) are effectively multiplied by N (or precisely by $Nz/2$ where z is the number of nearest neighbors). A cubic lattice is considered for the spin wave excitations. The displacement of the m-th ion is given by :

$$\delta R_m = \sum_k (\eta / 2NM\omega_k)^{1/2} i(a_{k'}^* - a_{-k}) \exp(ikR_m^0), \quad (11)$$

where a_k and a_k^* are phonon annihilation and creation operators, k = phonon wave vector, ω_k = frequency of phonon and M = atomic mass. The displacement δR_n of the n-th atom may be similarly expressed, and then one obtains that :

$$dR_{nm} = \sum_k (\eta / 2NM\omega_k)^{1/2} i(a_{k'}^* - a_{-k})[\exp(ika) - 1], \quad (12)$$

where $dR_{mn} = \delta R_n - \delta R_m$, and again the m-th ion is supposed to be at the origin *i.e.* $R_m^0 = 0$. The dynamic exchange or magnon-phonon interaction H_{mp} is obtained by using (10) and (12) in (9) as :

$$H_{mp} = -i(2J'S) \sum_{q,q',k} (\eta / 2NM\omega_k)^{1/2} [\exp(ika) - 1]$$

$$\times\ [\exp(-iqa) - 1]\ [\exp(iq'a) - 1] b_{q'}^* b_q\ (a_k^* - a_{-k}) \quad (13)$$

where the terms in phonon operators only (which do not represent magnon phonon coupling) have been dropped. It represents the 'two-magnon one-phonon' inelastic scattering process in which a magnon of wave vector q is annihilated and another magnon of wave vector q' is created with the emission (or absorption) of one phonon with wave vector k (or $-k$). This expression differs from the earlier ones [11,12] (though the methodology is similar) as it uses the general exchange term involving both q and q'. At low temperatures under long wavelength approximation (ka, $qa \ll 1$) one may use the simplified form :

$$[\exp(ika) - 1]\ [\exp(-iqa) - 1]\ [\exp(iq'a) - 1]$$

$$= ikqq'a^3. \quad (14)$$

Then the expression (13) reduces to :

$$H_{mp} = \sum_{q,k} C(q,k) \left[b_{q-k}^* b_q (a_k^* - a_k) \right], \quad (15)$$

where,

$$C(q,k) = (2SJ'a^3)(\hbar / 2NM\omega_k)^{1/2} q(q-k)k \quad (16)$$

4. Transition probability

The eigenstates are expressed in terms of the product of magnon and phonon occupation numbers, like $\Psi_i = |\ n_q, n_{q-k}, N_k >$, $E = E_i$ and $\Psi_f = |\ n_q', n_{q-k}', N_k' >$, $E = E_f$ for the initial and final states where n and N refer to magnon and phonon occupation numbers given by their Bose-Einstein distribution. The transition probability (W) is :

$$W = (2\pi/\hbar)\ |\ <\Psi_i|\ H_{mp}\ |\ \Psi_f>|^2 \delta(E_i - E_f). \quad (17)$$

It gives the change in the number of phonons per unit time. The difference of transition probabilities in two directions yields :

$$< \dot{N}_k > = (2\pi/\eta) \sum_{q,k} |C(q,k)|^2 \left[(n_{q-k} + 1) n_q \right]$$

$$(N_k + 1) - n_{q-k}(n_q + 1) N_k] \delta(E_{q-k} - E_q + E_k). \quad (18)$$

The delta function ensures energy conservation. The rate of transfer of energy between magnon and phonon sub-systems is given by :

$$\dot{Q} = \sum \eta\omega_k < \dot{N}_k > . \quad (19)$$

It is implied that the magnon and phonon sub-systems have different temperatures usually known as spin temperature (T_S) and lattice temperature (T). This means that n_q and N_k are expressed in terms of T_S and T respectively. Assuming that $T_S - T = \Delta T$ is small, one writes :

$$\exp(E_q/k_BT_S) = \exp(E_q/k_BT)[1 - (E_q/k_BT^2)\Delta T]$$

as per Taylor series method and also similarly for $\exp(E_{q-k}/k_BT_S)$. Using $E_q - E_{q-k} = E_k = \hbar\omega_k$ and for continuous magnon and phonon spectra :

$$\dot{Q} = (2\pi/\hbar)\int\int dqdk\ |C(q,k)|^2(\hbar\omega_k)^2 \times (\Delta T/ k_BT^2)\exp(E_q/k_BT)\ g(k)\ g(q)\delta(E_q - E_{q-k} - E_k) / [\exp(E_{q-k}/k_BT) - 1][\exp(E_q/k_BT) - 1] [\exp(E_k/k_BT) - 1] \quad (20)$$

where in denominator $T = T_S$ is used for magnons, and $g(k)$, $g(q)$ are density of phonon and magnon states. For a Debye lattice $g(k)\,dk = 3(Na^3/2\pi^2)\,k^2\,dk$ and $g(q)\,dq = (Na^3/2\pi^2)\,q^2\,dq$, where Na^3 is the volume (V) of the crystal and the factor 3 in $g(k)$ accounts for three directions of polarization. The exchange of energy between magnon and phonon sub-systems are related through :

$$dT/dt = Q/C_p \quad \text{and} \quad dT_S/dt = -Q/C_m, \quad (21)$$

where C_p, C_m are the specific heats of phonon and magnon sub-systems. A relation like $d(T - T_S)/dt = \Delta T/\delta t = \Delta T/\tau_{mp}$ means that the energy exchange happens within a time interval δt or the relaxation time τ_{mp}. Thus, relation (21) shows that [11] :

$$1/\tau_{mp} = [(1/C_m) + (1/C_p)]\ (Q/\Delta T). \quad (22)$$

5. Superparamagnetic particles

This formalism applies to any magnetic system while the difference lies in its magnetic energy. It consists of exchange, anisotropy, Zeeman and magnon (thermal excitation) terms. Magnon energy for ferromagnetic spin waves [14] is given by :

$$E_s = \sum_q (2J_0Sq^2a^2)b_q^*b_q = \sum (k_BT_Cq^2a^2)b_q^*b_q .$$

In terms of Curie temperature (θ_C), the exchange constant $J_0 = 3k_B\theta_C/2zS(S + 1)$ [15]. Here we use $T_C = 3\theta_C/z(S + 1)$ and it is seen that $T_C = \theta_C$ for $z = 2$, $S = 1/2$. For Fe(3+) in octahedral coordination ($S = 5/2$, $z = 6$) one gets $T_C = \theta_C/7$.

The particle energy given by (1) is also to be expressed in magnon operators. For the total spin $\boldsymbol{S} = NS$, we have $\boldsymbol{S}^2 = NS\ (NS + 1) \approx (NS)^2$ and $\boldsymbol{S}_z = NS - \sum_q b_q^*\ b_q$ so that :

$$\cos^2\theta = (S_z/S)^2 \approx 1 - (2/NS)\sum_q b_q^* b_q ,$$

neglecting $(b_q^*b_q)^2$. Then expression (1) gives :

$$E = -A_0 + B_0\sum_q b_q^* b_q ,$$

where $A_0 = (KV + g\beta_eHNS)$ and $B_0 = (2KV/NS + g\beta_eH)$. The fully ordered state with no magnons has energy $-A_0$ which is the depth of the anisotropy potential well and its value is equal to $-KV$ when no magnetic field is applied. Thus the total energy (E_q) of the magnon sub-system (or particle) at a finite temperature is given by :

$$E = -A_0 + \sum [B_0 + k_BT_Cq^2a^2]\ b_q^*b_q . \quad (23)$$

The energy of phonon sub-system (E_p) is given by the relation [15] :

$$E_p = \sum E_k a_k^* a_k = \sum (k_BT_DKa)a_k^* a_k . \quad (24)$$

where $T_D = \theta_D/(6\pi^2)^{1/3} \approx \theta_D/4$, and θ_D is the Debye temperature of the crystal.

6. Evaluation of $\dot{Q}$

Using the values of $C(k,q)$, $g(k)$, $g(q)$ and $\hbar\omega_k = k_BT_D ka$, the expression (20) gives :

$$\dot{Q} = (3N\hbar/4M\pi^3)\ (2J'S)^2\ (T_D\Delta T/T^2)\int\int dqdkq^4 (q - k)^2\ k^5\ a^{13} \times f(E_q)\ f(E_{q-k})\ f(E_k) \exp(E_q/k_BT)\ \delta(E_q - E_{q-k} - E_k) \quad (25)$$

where $f(E) = [\exp(E/k_BT) - 1]^{-1}$ is the Bose-Einstein distribution for magnons and phonons of respective energies. Using the dimensionless variables $x = ka$ and y

qa, the above integral reduces to :

$$\int\int dydx\, y^4(y - x)^2\, x^5 f(E_q)\, f(E_{q-k})\, f(E_k)$$

$$\exp(E_q/k_BT)\ \delta(E_q - E_{q-k} - E_k) \qquad \text{(I-1)}$$

The delta function in terms of $Eq = k_BT_C\, y^2$, $E_{q-k} = k_BT_C\, (y - x)^2$ and $E_k = k_BT_D\, x$ can be written as :

$$\delta(E_q - E_{q-k} - E_k) = (1/2\ k_BT_C\, x)\ \delta(y - (x + \alpha)/2),$$

where $\alpha = T_D/T_C$. The integration over y yields a non-zero value for $y = (x + \alpha)/2$ only giving :

$$(1/2^7 k_BT_C)\int dx x^4\, (x + \alpha)^4\ (x - \alpha)^2 f(E_q)$$

$$f(E_{q-k}) f(E_k)\ \exp(E_q/k_BT). \qquad \text{(I-2)}$$

This integral cannot be solved in a closed manner. At low temperatures x, y will be small and so the approximations $(x + \alpha) \to \alpha$, $(x - \alpha) \to -\alpha$, $f(E_{q-k}) \to f(E_q)$ and $f(E_q) \approx \exp(-E_q/k_BT)$ may be used. Then (I-2) contains only one $\exp(-E_q/k_BT) \approx \exp(-A)\ \exp(-B)\ \exp(-T_D^2/4TT_C)$ for the condition $y = (x + \alpha)/2 \to \alpha/2$, where $A = A_0/k_BT$ and $B = B_0/k_BT$. As $\exp(-E_q/k_BT)$ does not contain x, it comes out of the integral and (I-2) reduces to :

$$(1/2^7 k_BT_C)\ (\alpha^6)\ \exp(-T_D^2/4TT_C)\ \exp(-A)\ \exp(-B)\int dx$$

$$x^4\ [\exp(xT_D/T) - 1]^{-1}. \qquad \text{(I-3)}$$

This integral on phonon spectrum is evaluated at low temperatures within the limits 0 to ∞ as :

$$\int dx\, x^4\ [\exp(xT_D/T) - 1]^{-1} = (T/T_D)^5 \int dz\, z^4$$

$$[\exp(z) - 1]^{-1} = (T/T_D)^5\ [\,4!\ \zeta(5)] \qquad \text{(I-4)}$$

where the Riemann zeta function $\zeta(5) = 1.0369 \approx 1$. The expression (25) is finally given by :

$$\dot{Q} = (9N\hbar/64M\pi^2)\ (2J'S)^2\ (T_D^2/T_C^7)\ (T^3)\ (\Delta T/k_B)$$

$$\exp(-T_D^2/4T_CT)\ \exp(-A)\ \exp(-B) \qquad (26)$$

Since $A \gg B$ it is only the $\exp(-A)$ term which is effectively retained, that is, $\exp(-B) \approx 1$. This is a new result which differs from the earlier [11,12].

7. Expression for relaxation rate

The magnon specific heat (C_m) and phonon specific heat (C_p) are given by [14,15] :

$$C_m = 0.113\ Nk_B\ (T/\theta_C)^{3/2}, \qquad (27a)$$

$$C_p = (12\ \pi^4 Nk_B/5)\ (T/\theta_D)^3. \qquad (27b)$$

Using the values of $\dot{Q}$, C_m and C_p in (22) the superparamagnetic relaxation rate is given by :

$$1/\tau_{sp} = R_0(T)\ \exp(-A), \qquad (28a)$$

where

$$R_0(T) = (9\hbar/64M\pi^2)\ (2J'S)^2\ (T_D^2/T_C^7)\ (T^3/k_B^2)$$

$$\exp(-T_D^2/4T_CT) \times [8.85(\theta_C/T)^{3/2}$$

$$+ (5/12\pi^4)(\theta_D/T)^3]. \qquad (28b)$$

The pre-exponential factor $R_0(T)$ has remained almost unexplored, while it is very important in superparamagnetic relaxation theory. It is seen that $R_0(T)$ is substantially temperature dependent in a complicated manner.

8. Estimation of relaxation rates

Calculation of $1/\tau_{sp}$ requires many parameters, like θ_D, θ_C, K and J' for iron oxides, which can be estimated from experimental data. These magnetic systems are antiferromagnetic (goethite), weakly ferromagnetic (α-Fe_2O_3), ferrimagnetic (Fe_3O_4) or of uncertain magnetic structure (ferryhydrite). Surface effects may further complicate magnetic structure and lead to partial spin ordering. In general each magnetic structure may have a different dispersion relation of its own. These considerations simply indicate the difficulty in dealing with the problem in a quantitative manner.

It is assumed that ultra-fine iron oxide particles are essentially antiferromagnetic and the exchange coupling is strong. In this situation, the relaxation of the antiferromagnetic moment will be similar to that of the ferromagnetic moment in zero applied field. For α-Fe_2O_3 lattice $\theta_D \sim 700$ K [16], $\theta_C \sim 950$ K [17] and for Fe_3O_4 lattice $\theta_D \sim 650$ K [16], $\theta_C \sim 850$ K [18]. So $\theta_D \approx 700$ K and $\theta_C \approx 900$ K may be taken as their representative values. Their lattice constant $a \approx 5$ Å for which the unit cell volume $a^3 = V/N \approx 1.25 \times 10^{-22}$ cm^3 (sc structure). For Fe(3+), $M = 56 \times 1.66 \times 10^{-24}$ gm and $S = 5/2$.

The magnetic anisotropy energy has been measured in ferrous and ferric compounds like pyrrhotite (FeS to Fe_6S_7) and magnetite (Fe_3O_4). For cubic magnetite the anisotropy constant $K \approx 10^5$ erg cm^{-3} and for hexagonal pyrrhotite $K = 2 \times 10^5$ to 5×10^6 erg cm^{-3} depending upon the direction of magnetization [18]. Though these measurements have been made on bulk materials, it may not be unreasonable to assume a similar value of anisotropy

constant for small particles too if the anisotropy arises mainly from the microscopic interactions such as spin-orbit, exchange, dipolar and crystal field interactions [18]. For very small particles the non-symmetrical shape and surface effects can appreciably contribute to the anisotropy energy, but these may not change its order of magnitude. Here, we take $K \approx 10^5$ erg cm^{-3}, which translates into $K \approx 1.25 \times 10^{-17}$ erg or ≈ 0.1 Kelvin per magnetic ion.

The exchange constant (J) for iron compounds has been estimated as 0.27 eV by Koide *et al* [19] but taken as 0.1 eV [14]. For ferromagnetic iron ($S = 1$, $\theta_C = 1040$ K) the value of J comes to 0.012 eV through the standard relation which connects these quantities [15]. The iron oxides with a smaller Curie temperature and higher ionic spin suggest a lower exchange constant. For ferrimagnetic Fe_3O_4 $J \approx 21$ K or 2.0×10^{-3} eV [20] and a few other Fe-based ferrimagnets also give similar values [21]. It is therefore realistic to take $J \approx 2.0 \times 10^{-3}$ eV for ultra-fine iron oxides.

The dynamic exchange constant (J') may depend on the electronic orbitals which provide bonding. Here it is the $3d_z^2$ orbital of Fe(3+) and the $2p_z$ orbital of the oxygen ligand which provide most of the bonding and so the displacements within (O-Fe-O) along z direction produce most of the oscillating crystal field, which admixes the empty $4p$-orbital into the $3d$-orbital of Fe(3+) for an odd vibration. The potential energy of an electron at Fe ion of the collinear O-Fe-O chain may be taken as $V = (-Ze^2)[(R_0 - r)^{-1} + (R_0 + r)^{-1}]$, where R_0 is the equilibrium separation of O from Fe and r is the position coordinate of the electron with respect to the central Fe ion with charge + Ze. This gives $(dV/dR) = (dV/dr) = (4Ze^2r/R_0^3)$. Using $r \approx 1$ Å as the mean radius of a $3d$-orbital and $R_0 \approx 2.5$ Å, gives $dV/dr = 1.77 \times 10^{-3}$ erg cm^{-1}, which equals to $\langle 3d_{z^2} | dV/dR | 4p_z \rangle$ within an order of magnitude [12].

The value $E_\alpha - E_\beta$ (or $E_{3d} - E_{4p}$) for Fe-series metals lies in the range 5 to 10 eV but it has been considered safe to take $E_{3d} - E_{4p} \approx 10$ eV for iron [12] and it is taken here. Using the above estimates, one finds that $J' = 2.12 \times 10^{-6}$ erg cm^{-1}. The value of J' may change significantly in different systems and hence the above value provides only an initial estimate. For structurally similar oxygen bridged copper compounds, the estimated $J' = 5 \times 10^{-5}$ erg cm^{-1} [22] which shows that the above estimate is reasonable within an order of magnitude.

The relaxation rates have been calculated for $J' = 2.12 \times 10^{-6}$ erg cm^{-1}, $\theta_D = 700$ K, $\theta_C = 900$ K, ($T_c = \theta_C/7$, $T_D = \theta_D/4$) $S = 2.5$, $K = 10^5$ erg cm^{-3} and the number of Fe ions $N = 500$, 3000 and 7000 (or particles of size 49, 90 and 118 Å in diameter) respectively which cover the usual range of ultra-fine particles. The particle size has been expressed in terms of diameter assuming spherical shape. The calculated values are given in Table 1.

Table 1. Magnetic relaxation rate for iron oxide particles of different sizes at low temperatures.

T(K)	R_0 (sec^{-1})	$1/\tau_{sp}$ (sec^{-1})		
20	5.8×10^{10}	6.1×10^{9}	7.4×10^{4}	1.0×10^{3}
40	7.0×10^{11}	2.2×10^{11}	7.8×10^{8}	9.2×10^{4}
60	2.1×10^{12}	9.8×10^{11}	2.2×10^{10}	5.4×10^{7}
80	4.1×10^{12}	2.3×10^{12}	1.4×10^{11}	1.5×10^{9}
100	6.6×10^{12}	4.2×10^{12}	4.4×10^{11}	1.2×10^{10}
		N = 500	3000	7000
Particle Size (Å)		49	90	118

The table indicates that particles of around 49 Å may show magnetic spectra below 20 K while particles of size 118 Å may show magnetic spectra up to about 80 K, when the magnetic relaxation rate lies within the Mössbauer timescale window of 10^7 to 10^9 sec^{-1} [23,24]. This is generally in agreement with the experiments on many systems including those described above [1–3]. The model presented here provides a credible microscopic framework for the superparamagnetic relaxation and it is expected to supplement the study of nano-particles through other techniques.

References

[1] W Kundig, H Bommel, G Constabaris and R H Lindquist *Phys Rev.* **142** 327 (1966)

[2] S Morup and H Topsoe *J. Appl. Phys.* **11** 63 (1976)

[3] J Chadwick, D H Jones, M F Thomas, G J Tatlock and R W Devenish *J. Mag. Mag. Mater.* **60** (1986)

[4] W F Brown (Jr.) *Phys. Rev.* **130** 1677 (1963)

[5] A Aharoni *Phys. Rev.* **177** 793 (1969)

[6] I S Jacobs and C P Bean in *Magnetism* **Vol. III**, (eds.) George T Rado and Harry Suhl p 271 (New York : Academic Press) (1963)

[7] D H Jones and K K P Srivastava *Phys. Rev.* **B34** 7542 (1986)

[8] M Blume and T A Jons *Phys. Rev.* **165** 446 (1968)

[9] K K P Srivastava and D H Jones *Hyperfine Int. (Holland)* **42** 1047 (1988)

[10] D H Jones and K K P Srivastava *J. Mag. Mag. Mater.* **78** 320 (1989)

[11] A I Akhiezer *J. Phys. (Moscow)* **10** 217 (1946)

[12] K P Sinha and U N Upadhyaya *Phys. Rev.* **127** 432 (1962)

[13] T Holstein and H Primakoff *Phys. Rev.* **58** 1098 (1940)

[14] C Kittel *Quantum Theory of Solids* (New York : John Wiley) (1963)

[15] C Kittel *Introduction to Solid State Physics* 4th Edn. (New York : John Wiley) (1971)

[16] O L Anderson *Physicsl Accoustics* **Vol. III**, Part B P89 (New York : Academic) (1965)

[17] F Van der Woude *Phys. Stat. Solidi* **17** 417 (1966)

[18] R M Bozorth *Ferromagnetism* (New York : D Van Nostrand) (1951)

[19] S Koide, K P Sinha and Y Tanabe *Prog. Theor Phys* **22** 647 (1959)

[20] L Neel *Ann Phys* **3** 137 (1948)

[21] J Samuel Smart in *Magnetism*, **Vol. III** (eds) George T Rado and Harry Suhl p104 (New York : Academic) (1963)

[22] M Melnik *Co ordination Chemistry Reviews* **42** 259 (1982)

[23] H H Wickman *Mössbauer Effect Methodology* **2** 39 (1966)

[24] K K P Srivastava *J Phys* **C16** L53 (1983)